p-wave pairing in metals

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It is argued that for most metals the pairing force is not much weaker for Cooper pairs in a p state than in the conventional s state. Because in an antisymmetric p state the short-range Coulomb repulsion is not effective, p-wave pairing can be under certain circumstances, energetically favorable. A theory for pair breaking by impurity scattering is presented and it is concluded that p-wave superconductivity should be observable in a number of very pure metals such as Rh, W, Pd.

I. INTRODUCTION

An efficient way of constructing a theory of the superconducting transition temperature T_c is to consider the electron-electron scattering vertex $\Gamma(T)$ which describes the exchange of a phonon between two electrons in the normal state of the metal and seek the temperature T_c where $\Gamma(T)$ diverges.[1] Since $\Gamma(T)$ plays the role of a particle-particle scattering amplitude a divergence in $\Gamma(T)$ may be interpreted as being due to the appearance of a bound state: that is to say, at T_c two electrons at the Fermi energy ϵ_F can form a bound pair with energy less than $2\epsilon_F$. This instability leads to the superconducting state. A divergence in the s channel leads to the conventional BCS state. We shall assume that a divergence in the p channel signals the transition to a superconducting state where the Cooper pairs have a relative angular momentum $l=1$ in units of h.[2,3]

II. p-WAVE SUPERCONDUCTING TRANSITION TEMPERATURE T_c

We consider two electrons with a stationary center of mass and total energy which, when measured from ϵ_F, is zero. We then describe the scattering process taking the pair from the state $|\vec{k}, -\vec{k}\rangle$ to the state $|\vec{k}', -\vec{k}'\rangle$ by the scattering vertex function $\Gamma(\vec{k}, \vec{k}'; \epsilon_n - \epsilon_{n'})$. At the discrete imaginary frequencies $\epsilon_n = i\beta^{-1}\pi(2n+1)$, $\Gamma(\vec{k}, \vec{k}'; \epsilon_n - \epsilon_{n'})$ is determined by the following difference integral equation:

$$\Gamma(\vec{k}, \vec{k}'; \epsilon_n - \epsilon_{n'}) = I(\vec{k}, \vec{k}'; \epsilon_n - \epsilon_{n'}) - \beta^{-1} \sum_{n''} (2\pi)^{-3} \int d^3k'' I(\vec{k}, \vec{k}''; \epsilon_n - \epsilon_{n''}) G(\vec{k}'', \epsilon_{n''}) G(-\vec{k}'', -\epsilon_{n''}) \Gamma(\vec{k}'', \vec{k}'; \epsilon_{n''} - \epsilon_{n'}), \tag{1}$$

where $G(\vec{k}, \epsilon_n)$ is a finite-temperature one-particle Green's function for Bloch electrons renormalized by the electron-phonon interactions, and the irreducible scattering kernel $I(\vec{k}, \vec{k}'; \epsilon_n - \epsilon_{n'})$ is that appropriate to the exchange of one phonon.[1] In deriving Eq. (1) it was assumed that $I(\vec{k}, \vec{k}'; \epsilon_n - \epsilon_{n'})$ does not depend on the spin orientations of the scattering electrons and the spin variables have been eliminated from the problem.

Let us describe the electron-phonon interaction by the Hamiltonian

$$H_{\text{int}} = \sum_{\vec{k}, \vec{k}'; \nu} g_{\vec{k}, \vec{k}'; \nu} a^\dagger_{\vec{k}} a_{\vec{k}'} (b_{\vec{k}-\vec{k}'; \nu} + b^\dagger_{\vec{k}'-\vec{k}; \nu}),$$

where $a^\dagger_{\vec{k}}, a_{\vec{k}}$ create and annihilate Bloch electrons and $b^\dagger_{q;\nu}, b_{q;\nu}$ create and annihilate phonons with wave vector $\vec{q}$ and mode index ν, respectively. Furthermore, assume that $I(\vec{k}, \vec{k}'; \epsilon_n - \epsilon_{n'})$ only depends on the angle between $\vec{k}$ and $\vec{k}'$. Then, to a useful approximation, we may write

$$I(\mathrm{k}, \mathrm{k}'; \epsilon_n - \epsilon_{n'}) = \begin{cases} \sum_l I_l P_l(\hat{k} \cdot \hat{k}') & \text{for } |\epsilon_n - \epsilon_{n'}| \leq h\omega_c, \\ 0 & \text{otherwise,} \end{cases} \tag{2}$$

where ω_c is a cutoff frequency and

$$I_l = -\sum_\nu \int \frac{d^2k}{v_F} \int \frac{d^2k'}{v_{F'}} |g_{\vec{k}, \vec{k}'; \nu}|^2 \frac{2}{\omega_{\vec{k}-\vec{k}'; \nu}} P_l(\vec{k} \cdot \vec{k}') \times \left(\int \frac{d^2k}{v_F} \int \frac{d^2k'}{v_{F'}} \right)^{-1}. \tag{3}$$

Note that in this approximation the s-wave part of the effective electron-electron interaction $I_{l=0}$ is always attractive. However, for $l>0$, I_l may be negative or positive depending on the band structure.

We may further assume that $\Gamma(\vec{k},\vec{k}';\epsilon_n-\epsilon_{n'})$ will also have the form given in Eq. (3). This assumption defines Γ_l. We can now derive, from Eq. (1), an algebraic expression for Γ_l and show that the temperature where it diverges is given by

$$T_{c,l}=(\Theta_D/1.45)\exp[-(1+\lambda_0)\lambda_l^{-1}], \tag{4}$$

where Θ_D is the Debye temperature and $\lambda_l = -n(\epsilon_F)I_l$. The prefactor on the right hand side of Eq. (4) differs from its BCS value of $1.14\Theta_D$ only because we have chosen the cutoff frequency ω_c so that this factor would agree with McMillan's solution of the strong-coupling gap equations[4]

$$T_{c,0}=\frac{\Theta_D}{1.45}\exp\left(\frac{-1.04(1+\lambda_0)}{\lambda_0-\mu^*(1+0.62\lambda_0)}\right), \tag{5}$$

where μ^* is a pseudopotential designed to describe Coulomb repulsion between the electrons.

Note now that for $l=0$ Eq. (4) agrees well with the well-tested[4] result given in Eq. (5) except for the neglect of the Coulomb repulsion between the electrons in our theory. Of course we are interested in Eq. (4) for $l=1$. One might then be tempted to think that here too Eq. (4) should be corrected by a term analogous to μ^* in Eq. (5). However, a moment's reflection will reveal that this is not the case. In an antisymmetric p state the probability amplitude that members of a Cooper pair are at the same spatial point is zero. Because the Coulomb interaction between the two electrons is well screened and therefore short ranged in the p state the repulsion will be much less effective than in the symmetric s state. Therefore, in discussing $T_{c,l}$ we shall use Eq. (4) as it stands for $l=1$ but use Eq. (5) for $l=0$.

III. ESTIMATING $T_{c,1}$

We now want to estimate λ_1 and calculate $T_{c,1}$ from Eq. (4). To do this we recall that, to a reasonable approximation, the high-temperature resistivity of a solid may be written as[5]

$$R=\frac{6\pi k_B T}{e^2\hbar}\sum_{n,\nu}\int\frac{d^2k}{v_F}\int\frac{d^2k'}{v_F'}|g_{\vec{k},\vec{k}';\nu}|\frac{1}{\omega_{\vec{k}-\vec{k}';\nu}}|\vec{v}_n(\vec{k})-\vec{v}_n(k')|^2\left(\sum_n\int\frac{d^2k}{v_F}\vec{v}_n^2(\vec{k})\right)^{-2}, \tag{6}$$

where $\vec{v}_n(\vec{k})=\hbar^{-1}\vec{\nabla}\epsilon_{k,n}$ and the other symbols have their conventional meanings. Note now that if we make an effective-spherical-Fermi-surface approximation by taking $|\vec{v}_n(\vec{k})-v_n(\vec{k}')|^2 = \langle v^2\rangle(1-\hat{k}\cdot\hat{k}')$, with $\langle v^2\rangle$ defined as the average of $\vec{v}_n^2(\vec{k})$ over the Fermi surface, R may be written as a linear combination of λ_0 and λ_1. In fact we find that

$$\lambda_1=\lambda_0-(4k_B)^{-1}\hbar\omega_p^2\left(\frac{dR}{dT}\right)_{T>\Theta_D}^{-1}, \tag{7}$$

where the plasma frequency is defined by

$$\omega_p^2=\tfrac{4}{3}\pi e^2\sum_{\vec{k},n}\vec{v}_n^2(\vec{k})\delta(\epsilon_F-\epsilon_{\vec{k},n}).$$

Our estimates of λ_1 and $T_{c,1}$ using Eqs. (4) and (7) are shown in Table I. For superconductors λ_0 was obtained from measured values of $T_{c,0}$. For Pd we used a calculated value.[8] We took $(dR/dT)_{T>\Theta_D}$ and ω_p^2 from experiments.

Admittedly Eq. (7) represents only a rough approximation for λ_1. Nevertheless, we may conclude from Table I as a whole that while λ_1 is always smaller than λ_0 it is reasonable to expect that for a number of metals $T_{c,1}$ is of the order of 1 K.

Of course we may expect to observe p-wave superconductivity only if $T_{c,1}>T_{c,0}$. To clarify how such a situation may arise in our calculation we calculated $T_{c,0}$ from Eq. (5) using the same values of Θ_D and λ_0 as in our calculation for $T_{c,1}$. As is customary we took $\mu^*=0.13$ for transition metals. The results are shown in Table I. Evidently, the decrease in λ on going from $l=0$ to $l=1$ is frequently overcompensated by μ^* being zero in our formula for $T_{c,1}$. In physical terms this implies that though the pairing force is less effective in a

TABLE I. Values of parameters involved in estimating λ_1, and results for λ_1, $T_{c,1}$, and α for a number of transition metals. For explanation and discussion see text.

	λ_0	ω_p (eV)	$\left(\frac{dR}{dT}\right)_{T>\Theta_0}$ ($\mu\Omega$/K)[j]	λ_1	$T_{c,1}$	$T_{c,0}$	α ($\times10^3$)
Nb	0.82[a]	9.1[d]	0.04	0.409	1.94	8.00	3
Mo	0.41[a]	7.4[d]	0.027	0.226	0.61	0.84	1.3
W	0.29[a]	5.04[e]	0.029	0.199	0.41	0.01	1.3
Pd	0.31[b]	5.63[f]	0.030	0.192	0.20	0.028	4.7
		2.80[g]		0.280	1.7		
Ir	0.37[c]	3.6[h]	0.028	0.325	4.32	0.33	1.8
Rh	0.44[c]	5.2[i]	0.025	0.356	5.80	1.42	2.1

[a] See Ref. 6.
[b] See Ref. 7.
[c] See Ref. 8.
[d] See Ref. 9.
[e] See Ref. 10.
[f] See Ref. 11.
[g] See Ref. 12.
[h] See Ref. 13.
[i] See Ref. 14.
[j] See Ref. 15.

p state than in an s state the lack of Coulomb repulsion in the former might make the formation of Cooper pairs in the p state energetically more favorable. Clearly, the role played by the core repulsion between ^{3}He particles in superfluid ^{3}He is entirely analogous to the above effect.[3] Also, Appel and Heyszenau[16] had reached the same conclusions in the context of alkali metals. However their formula for $T_{c,1}$ involves the term $1+\lambda_1$ in place of $1+\lambda_0$ in Eq. (4). As this factor arises from the self-energy of the electrons which then scatter from each other, the expression $1+\lambda_0$ is clearly the appropriate one.

Of course, the case of Pd should be considered separately. Like ^{3}He Pd sustains long-lived paramagnetic spin fluctuations. These are believed to be responsible for the nonoccurrence of ordinary s-wave superconductivity in Pd.[17] However, they should enhance p-wave pairing.[18] Thus, $T_{c,1}$ in Table I for Pd should be bigger rather than smaller.

IV. EFFECTS OF IMPURITIES

Before attempting to assess whether p waves should be observable or not we must discuss the effects of impurity scattering on $T_{c,1}$. As has been frequently remarked[2] these are drastic and constitute the main obstacle to the occurrence of the phenomenon.

In the presence of a random arrangement of impurities the Green's function $G(\vec{k},\vec{k}';\epsilon_n)$ is no longer diagonal. Moreover, Eq. (1) must be replaced by one for the ensemble-averaged vertex part $\bar{\Gamma}(\vec{k},\vec{k}';\epsilon_n-\epsilon_{n'})$. Evidently, we must write

$$\bar{\Gamma}(\vec{k},\vec{k}';\epsilon_n-\epsilon_{n'}) = I(\vec{k},\vec{k}';\epsilon_n-\epsilon_{n'}) - \beta^{-1}\sum_{n''}(2\pi)^{-6}\int d^3k''\int d^3k'''\, I(\vec{k},\vec{k}'';\epsilon_n-\epsilon_{n''})\langle G(\vec{k}''\vec{k}''';\epsilon_{n''})G(-\vec{k}'',-\vec{k}''';-\epsilon_{n''})\rangle\bar{\Gamma}(\vec{k}''',\vec{k}';\epsilon_{n''}-\epsilon_{n'}). \tag{8}$$

Clearly, a theory for $\langle GG\rangle$ follows the usual arguments leading to a theory of impurity resistivity.[19] Assuming that $\bar{\Gamma}$ and I have the functional form of Eq. (2), in what might be called the relaxation-time approximation for $\langle GG\rangle$, we find from Eq. (8) that

$$\bar{\Gamma}_l = \bar{I}_l(1-\bar{I}_l\bar{F}_l)^{-1}, \tag{9}$$

where

$$\bar{F}_l = -\beta^{-1}\sum_{n=-\infty}^{\infty} 2\pi\bar{n}(\epsilon_F)[2(1+\lambda_0)\epsilon_n + \hbar(\tau_0^{-1}-\tau_l^{-1})]. \tag{10}$$

In Eq. (10) $\bar{n}(\epsilon_F)$ is the averaged density of states, which we assume to be practically the same as that for the pure system, and the various relaxation times are given by

$$\frac{1}{\tau_l} = \frac{2\pi}{\hbar}\frac{2l+1}{4n}\, c\int\frac{d^3k'}{(2n)^3}\left|t_{\vec{k},\vec{k}'}\right|^2 P_l(\vec{k}\cdot\vec{k}')\delta(\epsilon_{\vec{k}}-\epsilon_{\vec{k}'}), \tag{11}$$

where c is the concentration of the impurities and $t_{\vec{k},\vec{k}'}$ is the electron impurity scattering amplitude.

Note that the form of Eq. (10) also arises in the theory of magnetic impurities in superconductors.[20] The renormalization of the energy ϵ_n by the factor $1+\lambda_0$ is the mass-enhancement effect and $h(\tau_0^{-1}-\tau_l^{-1})$ is the pair-breaking parameter. Clearly for $l=0$ there is no pair breaking. This is the well-known result of Abrikosov and Gorkov.[10] However for $l=1$ there is pair breaking and the pair-breaking parameter is just the transport relaxation time $\tau_{tr}^{-1}=\tau_0^{-1}-\tau_1^{-1}$. For small concentrations it follows straightforwardly from Eqs. (9) and (10) that the reduction in $T_{c,1}$ due to this pair breaking is given by

$$T_{c,1} = T_{c,1}^0 - \hbar\pi(\tau_{tr})^{-1}. \tag{12}$$

The same expression was obtained by Larkin[21] using a slightly different method. Clearly, Eq. (12) sets a severe limit on the observability of p-wave superconductivity. Roughly speaking it says that the broadening of the electronic levels due to impurity scattering must be less than the expected gap $k_B T_{c,1}$, at best a few degrees.

The deep reason for such a fundamental difference between the behaviors of s- and p-wave superconductors in the presence of impurities is the difference in the time-reversal symmetry of the two states. Members of a pair with a finite relative angular momentum are not in states related to each other by a time-reversal transformation. As a consequence the Anderson theorem[6] does not hold and even nonmagnetic impurities act as pair breakers. In fact an observation of a transition temperature T_c which decreased linearly with concentration of nonmagnetic impurities could be taken as evidence for p-wave pairing. Note that anisotropy of the Fermi surface can also cause a linear decrease of T_c.[22] However, this is a two-orders-of-magnitude smaller effect and therefore it should

be possible to distinguish it from p-wave pairing on quantitative grounds.

To illustrate the practical significance of Eq. (12) we estimate the transport lifetime from the resistivity ratio $R_{273}/R_{4.2}$. In terms of this more easily available quantity we may rewrite Eq. (12) as

$$T_{c,1} = T^0_{c,1} - \alpha(R_{4.2}/R_{273}), \tag{13}$$

where α is a different constant for different metals. Our estimates of α are given in Table I. Thus we conclude that p-wave superconductivity should be observable in Pd, W, Rh for resistivity ratios between 10^3 and 10^5 even if our estimates of λ_1 are off by a factor of 2.

We note that for W $T_c = 15$ mK down to a resistivity ratio of 2×10^4.[23] This means that our estimate of $T^0_{c,1} = 0.41$ is too large by at least a factor of 6.3. However, according to Eq. (13) a $T^0_{c,1}$ of 65 mK would have gone undetected for such a resistivity ratio. The possibility of $T_{c,1} > T_{c,0}$ would be eliminated by experiments on samples with $2 \times 10^4 < R_{273}/R_{4.2} < 8 \times 10^4$. Clearly this fact has implications for thermometry using low-T_c materials.

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